

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 June 2002 (20.06.2002)

PCT

(10) International Publication Number
WO 02/48036 A1

(51) International Patent Classification⁷: **C01B 33/187**

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(21) International Application Number: **PCT/NO01/00428**

(22) International Filing Date: 29 October 2001 (29.10.2001)

(25) Filing Language: Norwegian

(26) Publication Language: English

(30) Priority Data:
20005521 2 November 2000 (02.11.2000) NO

(71) Applicant (for all designated States except US): **SILICA TECH ANS** [NO/NO]; Haakon VII's gate 2, P.O. Box 1364 Vika, N-0114 Oslo (NO).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HANSEN, Tord** [NO/NO]; Vakåsveien 52, N-1395 Hvalstad (NO). **ZANDER, Bo** [SE/SE]; S-711 77 Stråssa (SE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i)) for all designations
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/48036 A1

(54) Title: **EXTRACTION OF SILICA AND MAGNESIUM COMPOUNDS FROM OLIVINE**

(57) Abstract: A method is described for extraction of silica and magnesium compounds, by chemical and thermal treatment of the mineral olivine. The method comprises sulphating of olivine, where olivine is mixed with concentrated sulphuric acid at a weight ratio olivine/sulphuric acid of approx. 0.5-0.67, and by heating the mixture to approx. 250°C and giving the mixture a reaction time of approx. 8 hours, and thereafter dissolve the mixture in water, whereby silica precipitates to a solid and where the silica after filtration is purified in a weak solution of soda, and eventually with a weak aqueous solution of an acid or a mixture of acids. This method provides manufacturing of a purified silica solid, leaving a filtrate consisting mainly of dissolved magnesium which after further processing is transformed to magnesium compounds.

Extraction of Silica and Magnesium Compounds from Olivine.

Description of the invention

The present invention relates to a method for extraction of silica (SiO_2) and magnesium compounds (MgCO_3 , MgO , Mg(OH)_2 , MgSO_4 , MgCl_2) from the mineral olivine (Mg_2SiO_4) by chemical and thermal treatment.

The use of precipitated silica within filler markets, including plastic, paint, sealant and the rubber tire industry, has during the last ten years increased considerably. The total consumption of precipitated silica in world markets extends 1 million tons per year. And a continuing increase of consumption within the filler markets will result in a need of increased production capacity.

Concerning magnesium compounds is the refractory industry dominating consuming 65% of the total demand. Other important markets are the chemical industry, the water treatment sector and the use within different environmental areas. The total consumption of magnesium compounds is approx. 10 million tons of MgO per year. The magnesium metal industry is hereby only a modest consumer, with a demand of approx. 500.000 tons per year. The raw materials used for production of magnesium compounds are mainly magnesite (MgCO_3) counting for approx. 80% of the raw materials in use, while sea water (0.13% MgO)

The main consumption of precipitated silica in the world market is covered through complex production processes involving high investment and operating costs, resulting in a high cost product.

MgO in the refractory industry is mainly considered as a commodity product market where prices are based on offer and demand.

As possible interferences, the following patent documents have been examined :

- (1) NO 177137 (corresponding to " US Patent No 5,780,005 ")
- (2) NO 143583
- (3) NO 160200

(4) AT 352684

(5) JP 60161320

Examining the above listed patent documents, the methods described shows that the olivine minerals are leached in aqueous solutions of mineral acids in acid baths, involving that the dissolving process of the olivine mineral and the formation of silica takes place in an acid bath at a maximum temperature of 110°C. These methods involved results in the formation of a silica-gel, where a small part of solids binds a large volume of liquid. A main problem combined with a use of the known technology is the formation of silica-gel, which restricts or excludes efficient filtering and thereby excludes a practical use of technology.

The present invention is described by mixing ground olivine sand with concentrated sulphuric acid at a weight ratio olivine/sulphuric acid of 1-0.3, to a slurry, which by thermal treatment is heated to temperatures between 150°C - 400°C, ideally 250°C, over a period of time ranging between 3-12 hours, ideally 7-8 hours. This treatment may more precisely be characterized as a sulphating process. Combined with the thermal treatment, the mixture forms a dry aggregate product, which then is dissolved (leached) in water. It is hereby achieved to precipitate silica solids spontaneous without gel formation, where the rest solution consists of aqueous magnesium sulphate.

As described is the present invention of significant difference from other known technologies, first by the present treatment method which more precise is characterized as sulphating and where known technologies are presented as acid leaching, and second that the temperatures involved in the present sulphating process demands significant higher degrees compared with the known leaching methods. It is also of significance that the silica end product in the present invention results in the formation of a non gel silica, while the known methods results in silica gel formation which restricts a practical use of the methods. The examined patent documents are therefor not considered to be of relevant interference to the present invention.

The present invention concerns manufacturing of silica and magnesium compounds based on ground olivine, where the mineral olivine ideally is recommended to contain 48-50% MgO. The invention relates to a method for manufacturing silica (SiO_2) and magnesium compounds (MgO , MgCO_3 , Mg(OH)_2 , MgSO_4 , MgCl_2), based on the mineral olivine ($(\text{Fe,Mg})_2\text{SiO}_4$), characterized wherein olivine is mixed with concentrated sulphuric acid at a weight ratio olivine/sulphuric acid of 1 – 0.3, and by heating the mixture between 150°C – 400°C , giving the mixture a reaction time between 3 – 12 hours, and thereafter dissolve (leach) the mixture in water, whereby silica precipitates to a solid and then is removed from the solution by filtration, where the filtrate containing dissolved magnesium is further processed to magnesium compounds, and where the silica filter product is further washed with a weak solution of soda (NaCO_3) or sodium hydroxide (NaOH) and thereafter eventually further washing of the silica with a weak aqueous solution of an acid or a mixture of acids, in order to obtain a pure silica (solid) which is filtered out as a silica product.

It is hereby achieved to manufacture a silica product with significant identical characteristics compared to precipitated silica, through a relative simple process at a relative low cost.

After filtering out the silica solids, the rest solution is treated separately, which more specified is described by a first step neutralization of excess acid with ground limestone (CaCO_3), until a weak sour or neutral solution is obtained, whereby precipitated gypsum (CaSO_4) is filtered out. The rest solution is then treated by "solvent extraction" process (Elkem method) whereby iron (Fe) is removed from the solution. The rest solution is then blown through with CO_2 gas whereby MgCO_3 is precipitated and filtered out (Pattison method). MgCO_3 may then be transferred to calcination for manufacturing of MgO. The filtrate may then be transferred to a waste treatment plant eventually to a separate plant for manufacturing of nickel and chromium compounds.

Example

The starting material used was olivine sand AFS 120 (49-50% MgO) which was ground down to 70% minus 0.044mm in a ball mill. The material had the following chemical analysis:

SiO ₂	41.5 - 42.5%
Fe ₂ O ₃	6.8 - 7.3%
Cr ₂ O ₃	0.2 - 0.3%
Al ₂ O ₃	0.4 - 0.5%
NiO	0.3 - 0.35%
MnO	0.05 - 0.1%
CaO	0.05 - 0.1%
MgO	49.0 - 50.0%

The ground olivine sand was mixed with concentrated sulphuric acid (H₂SO₄) at a weight ratio olivine/sulphuric acid of 0.5 and heated to 250°C. The mixture was given a reaction time of 8 hours at a constant heat of 250°C. The sulphated mixture was then dissolved in water (approx. at 12 weight % solids) during a stirring period of 30 minutes. The solid silica product was thereafter filtered out, while the filtrate was stored in a separate container. The solid silica product was then mixed with a 5% soda solution at a weight of 12%. The purified silica product was thereafter filtered out while the restsolution was stored in a waste material container. The purified silica was then mixed with water (12% solids by weight) during a stirring period of 30 minutes as the last cleaning step. The purified silica was thereafter filtered off and dried. The rest solution was stored in a separate waste container. The dried silica product had the following analysis.

SiO ₂	96%
MgO	3.50%
BET	100 kv.m/g

The analysis shows that the silica product obtained can be identified and classified as precipitated silica. An additional cleaning step of the silica could involve further washing with a weak solution of a 1 – 2% HCL + HF, in order to dissolve excess impurities.

The restsolution from the first leaching step with water, which after filtering out the silica, leaves a solution containing mainly dissolved magnesium in addition to minor part of dissolved iron, chromium, nickel and aluminium together with excess sulphuric acid from the main reaction, is first neutralized with lime. Precipitated gypsum is filtered out, whereafter iron is extracted from the filtrate by the Elkem method. The filtrate then containing mainly

dissolved magnesium and minor parts of nickel, chromium and aluminium is treated with carbondioxide gas, resulting in formation of dissolved magnesium-bicarbonat ($\text{Mg}(\text{HCO}_3)_2$). Heating of the magnesium-bicarbonate solution, leads to formation of magnesium carbonate solids(Pattison method), which is filtered out and dried. The described process illustrates how production of syntetic magnesite (MgCO_3) takes place, which corresponds to the main material source for magnesium compounds.

Claims

We claim:

1. A method for manufacturing of silica (SiO_2) and magnesium compounds (MgO , MgCO_3 , $\text{Mg}(\text{OH})_2$, MgSO_4 , MgCl_2), based on the mineral olivine ($(\text{Fe,Mg})_2\text{SiO}_4$), *characterized* wherein olivine is mixed with concentrated sulphuric acid at a weight ratio olivine/sulphuric acid of 1 – 0.3 ,and by heating the mixture between 150°C - 400°C , and giving the mixture a reaction time between 3 – 12 hours, and thereafter dissolve (leach) the mixture in water, whereby silica precipitates to a solid and then is removed from the solution by filtration, where the filtrate containing dissolved magnesium is further processed to magnesium compounds, and where the silica filter product is further washed in a weak solution of soda (NaCO_3) or sodium hydroxide (NaOH) and thereafter eventually is further washed with a weak solution of an acid or a mixture of acids, in order to obtain a pure silica product.
2. The method of claim 1, *characterized* wherein the weight ratio olivine/sulphuric acid is between 0.5-0.67, and by heating the mixture up to 250°C , giving the mixture a reaction time of approx. 8 hours.
3. The method of claim 1, *characterized* wherein the filtered silica is purified by washing with a weak solution of hydrofluoric acid, eventually in a mixture with another mineral acid, as hydrochloric acid.
4. The method of claim 1, *characterized* wherein the filtered silica in one or more purification steps is treated with water dissolved peroxides, chlorates and ammonia.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 01/00428

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01B 33/187

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5780005 A (OLERUD), 14 July 1998 (14.07.98), figure 1, claim 1, abstract -- -----	1-4

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

28 February 2002

05-03-2002

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Moa Emling Grönkvist/ELY
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

28/01/02

International application No.

PCT/NO 01/00428

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5780005 A	14/07/98	AT 161522 T	15/01/98
		AU 7666894 A	27/03/95
		BR 9407389 A	29/10/96
		CA 2171099 A	16/03/95
		CN 1133586 A	16/10/96
		DE 69407610 D,T	09/04/98
		EP 0720587 A,B	10/07/96
		SE 0720587 T3	
		ES 2113124 T	16/04/98
		FI 961018 A	02/05/96
		GR 3026299 T	30/06/98
		JP 9502688 T	18/03/97
		NO 177137 B,C	18/04/95
		NO 933168 A	07/03/95
		PL 313351 A	24/06/96
		WO 9507235 A	16/03/95